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ENVIRONMENTAL RESEARCH BRIEF

Assessment of Natural Volatile Organic Substances and Their Effect on Air Quality in the United States

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Abstract

This research brief is a summary of the extensive review and critical analysis of the literature on natural volatile organic substances, sometimes referred to as biogenic hydrocarbons, and an assessment of that body of scientific information. The review is reported separately (Natural Volatile Organic Substances and Their Effect on Air Quality, submitted to Atmospheric Environment). The conclusion reached in this assessment is that there is a lack of evidence that natural hydrocarbons contribute substantially to the formation of ambient air concentrations of ozone.

Introduction

This assessment is based on a review document entitled "Natural Volatile Organic Substances and Their Effect on Air Quality" accepted for publication in *Atmospheric Environment*. The review considers sources of natural volatile organic substances, environmental effects on their emission rates, emission inventories, ambient air concentrations, lifetimes and their ambient air reaction products.

Six scientific issues were identified. A detailed discussion of each of these issues is contained in the review. In this research brief, each issue will be stated, its background briefly discussed, and the conclusions summarized. In addition, specific recommendations will be presented. (Additional recommendations are given in the Review.)

Issue 1. What are the relationships between anthropogenic and biogenic emission inventories and air quality measurements?

The biogenic emission inventory developed by Zimmerman (1979) predicts that 15 million metric tons of isoprene and

50 million tons of monoterpenes are emitted from the contiguous United States. The anthropogenic emissions of hydrocarbons for the United States are estimated to total at 27 million metric tons (U.S. Environmental Protection Agency, 1974). Therefore, it might be expected that isoprene and several of the monoterpenes would be measured in the ambient atmosphere at large excesses to individual anthropogenic hydrocarbons such as propene and acetylene. Based on the biogenic emission inventory for isoprene and the fraction on anthropogenic hydrocarbons as propene and acetylene, emission ratios of isoprene to propene or acetylene ranged from 27:1 to 70:1. In contrast, the ratios of ambient air concentrations at various study sites ranged from 1:1 to 9:1. The emission inventory results overpredict these ratios by factors of 7 to 35 compared to ambient air measurements. Various field studies also indicate low ambient air concentrations for α -pinene and other monoterpenes.

Among the possible causes for the large differences discussed above are the following: (1) The biogenic emission inventory is much too high. (2) The anthropogenic emission inventory is much too low. (3) The biogenic compounds react so rapidly in the atmosphere as to disappear before collection. (4) The biogenic compounds react rapidly with ozone in the sampling container. (5) Most of the biogenic compounds are lost to the walls of the containers used during the storage period before analysis.

Of the various possibilities discussed above, the most likely ones to explain the larger part of the discrepancies are those associated with the emission inventories. The other possibilities appear capable of only accounting for only a small portion of the differences in ratios between source inventories and ambient air concentrations. A combination of substantial under-estimates in the anthropogenic



emission inventory, along with a substantial overestimate in the biogenic emissions, appears necessary to account for these differences in ratios. Existence of a substantial underestimate in the anthropogenic inventories for volatile organic compounds would be of general concern with respect to implementation of ambient air standards for ozone. Therefore, any and all independent means of verifying anthropogenic inventories should be utilized. Since air quality simulation models used for implementation of standards start with emission inventories and not with ambient air concentrations of hydrocarbons, any substantial inventory errors could interfere with utilization of the air quality simulation models in developing control strategies.

Issue 2. Have biogenic species been adequately identified and quantitated?

There has been a concentration of effort on measurements of emissions from forest species. Only limited biogenic emission measurements are available on grasses and field crops. Tingey (1981) recently investigated emissions from beans, soybeans, corn and clovers and found these to have smaller emissions than trees. There also has been little work done on the emissions from the sclerophyll scrub species in California. Most investigators have not attempted to identify biogenic oxygenated species so results are limited for these types of compounds. Biogenic species have been adequately identified and perhaps quantitated for a number of hydrocarbons from a number of important forest species, but substantial gaps in information exist with respect to emissions from grasses, agricultural crops and soils.

Issue 3. How reliable is the bag enclosure technique for estimating the composition of emitted products?

Substantial differences in composition have been reported between investigators for the same species. In some instances, the differences may be associated with the completeness of the analytical measurements. Composition also may vary because of variations in emissions from different ecotypes and genotypes of the same species (Tingey, 1981). However, ambient air measurements in pine forests also appear to give different compositional results than do bag enclosure measurements (Arnts, et al, 1981). Therefore, the adequacy of compositional measurements from the bag enclosure techniques appears to be unclear.

Issue 4. How effective are biogenic hydrocarbons in contributing to the formation of ozone in the atmosphere and how does this potential compare with that of anthropogenic hydrocarbons?

The ozone-producing potential of isoprene and various monoterpenes do not exceed, and usually are less than, the potential associated with most anthropogenic hydrocarbons. Smog chamber results suggest that the ozone production from atmospheric mixtures of anthropogenic hydrocarbons should be in the range of 10 to 30 ppb of ozone produced per 100 ppbC of hydrocarbon consumed. Based on average concentrations of isoprene and monoterpenes measured at several rural sites, these biogenic hydrocarbons are estimated to be capable of producing from 0.1 to 0.7 ppb of ozone. The highest

isoprene concentrations measured during a stagnation (August 12, 1975) constituted from 5 to 20 percent of the total hydrocarbon measured at the rural site, Glasgow, IL (Rasmussen, et al, 1977). The α -pinene concentrations were low, 0.3 ppbC. Since α -pinene is less effective than isoprene in ozone production, its contribution can be ignored. The concentrations of isoprene present during this stagnation based on its smog chamber ozone production potential, might contribute from 2 to 10 ppb of ozone. The ozone peaked at 1900 at slightly over 100 ppb. Therefore, the biogenic hydrocarbons identified did not contribute a substantial part of the ozone observed.

It should be mentioned that higher concentrations of biogenic hydrocarbons occasionally have been measured. For example, Ferman (1980) measured over 150 ppb of isoprene as a maximum concentration at a site near Keysville, VA. The concentrations of ozone, nitrogen oxides or other hydrocarbons concurrently present were not reported. Rasmussen and Went (1965) observed unusually high concentrations at a rural site during leaf drops of forest species. It is possible under such circumstances, that biogenic hydrocarbons may make a more significant contribution to ozone formation.

Issue 5. What is the potential of paraffinic hydrocarbons from seepage losses through soil to participate in the formation of ozone?

Seepage losses through soil of paraffinic hydrocarbons may contribute ambient air concentrations capable of generating ozone concentrations in excess of those attributed to isoprene and monoterpenes. Because of the lack of sufficient measurements in the literature, it is not now possible to determine whether or not hydrocarbons from seepage through soil could account for a substantial part of the ozone observed downwind of gas- and petroleum-bearing areas.

Issue 6. What is the potential of biogenic hydrocarbons compared to anthropogenic emissions to participate in the formation of aerosols in the atmosphere?

Aromatic hydrocarbons have moderate aerosol-forming capabilities (Grosjean, 1977). In the review, based on the study by Miller and Joseph, 1976, it was estimated that aromatic hydrocarbons can generate on the average about 0.02 g m^{-3} of aerosol per ppmC of aromatic hydrocarbon. Monoterpenes appear to be very effective in producing organic aerosols. Laboratory studies show that the monoterpene, α -pinene, has an organic aerosol-forming potential about a factor of 5 to 10 times higher than aromatic hydrocarbons.

At a site in the Smoky Mountains, TN, (Arnts and Meeks, 1980) 20 ppbC of aromatics and 1 ppbC of α -pinene were measured. Applying the aerosol-forming potentials just discussed, about $0.4 \text{ } \mu\text{g m}^{-3}$ of organic aerosol can be attributed to reactions involving aromatic hydrocarbons and 0.1 to $0.2 \text{ } \mu\text{g m}^{-3}$ to reactions involving α -pinene. An estimate based on an independent approach in the review results in an estimate of $0.15 \text{ } \mu\text{g m}^{-3}$ of organic aerosol produced from α -pinene. No other monoterpene was detected. The sulfate concentrations have been measured at the Smoky Mountain site (Stevens, et al, 1980a) at a rural site in the Shenandoah Valley of Virginia (Stevens, et

al, 1980b) and at the Allegheny Mountain site in southwestern Pennsylvania (Pierson, *et al*, 1980). At these rural sites along the Appalachian Mountain chain the sulfates (as acid sulfates) were in the 14 to 16 $\mu\text{g m}^{-3}$ range. Clearly, the estimates of organic aerosol generated by observed α -pinene concentrations are insignificant compared to these sulfate concentrations. Based on these estimation procedures, even if the α -pinene concentration had been averaged 10 ppbC rather than 1 ppbC, the organic aerosol produced would only have been about 10 percent of the sulfate aerosol concentration.

It is concluded in the review that in the eastern United States the aerosols formed from monoterpenes are not likely to constitute a substantial fraction of the fine particle aerosol concentrations.

Conclusions

There is a lack of evidence in the literature that natural hydrocarbons contribute substantially to the formation of ambient air concentrations of ozone and aerosols. There is some evidence that very small amounts of ozone, less than 10 ppb, might form from atmospheric reactions of isoprene from natural sources with nitrogen oxides from anthropogenic sources. Within forest canopies where natural hydrocarbons are the most abundant, natural hydrocarbons are most likely to consume rather than form ozone. Even those investigators who contend that natural hydrocarbon emission rates are substantial have not provided evidence that substantial amounts of ozone are formed from the reactions of these hydrocarbons with nitrogen oxides.

It is possible that future work might substantiate high natural hydrocarbon emission rates, particularly for short intervals of time at specific locations. Even if such results should be obtained, it is not evident that inclusion of such results would be critical to the development of practical air quality models for ozone.

It is concluded that adequate justification does not exist at present to support the considerable effort needed to develop natural emission inventories for all areas of the United States.

Recommendations

1. The Zimmerman bag enclosure technique is still the only practical approach to obtaining emissions in the field for a variety of species. Since this technique has been shown to give substantially different emission rates than other techniques and to be inconsistent with ambient air measurements, its applicability in developing acceptable biogenic emission inventories is in question. If the results of the bag enclosure technique can be considered usable on a relative basis, a large upward gradient is predicted in emissions from higher to lower latitudes. The southern United States, including the Gulf Coast Region, is likely to have the highest emissions of biogenic hydrocarbon emissions. If a biogenic emission inventory is to be included in air quality models for ozone, it would be more appropriate to consider doing so in the southern United States rather than elsewhere.
2. A fundamental difficulty in developing a biogenic emission inventory by any technique is the wide

variability in these emissions. The emissions rates are functions of temperature and light intensity. There may be growing season effects for field crops. Lead drop from trees also has been reported to increase emissions. Therefore, the possibility exists for excursions to high emission levels for short time periods. This problem also limits the usefulness of seasonal biogenic emission inventories. Therefore, it does not appear useful to develop annual inventories of natural hydrocarbons for the U.S. Because a substantial fraction of U.S. emissions of natural hydrocarbons is estimated to occur in the warmer months of the year in the southeastern United States, an improved emission inventory should be developed for this area.

3. The magnitude of these short time biogenic emission effects has received little attention. A number of the aspects involved could be investigated in local forested areas.
4. Because of the small amount of effort expended on study of biogenic oxygenated hydrocarbons, it is possible that their contributions to the total biogenic emissions are being underestimated. Some additional measurements on these types of compounds in the southern United States would be appropriate.
5. One of the explanations for the much lower ratios of biogenic to anthropogenic hydrocarbons from ambient air measurements compared to biogenic emission measurements is a serious underestimation of anthropogenic emissions. The techniques for estimating anthropogenic emissions should be carefully reviewed.
6. One additional source of hydrocarbons not included in anthropogenic emission inventories nor in current biogenic inventories is seepage losses of paraffinic hydrocarbons. Only a few measurements related to seepage losses are available. Since gas- and petroleum-bearing formation cover substantial on-shore and off-shore areas of the United States, additional ambient air measurements would be desirable in selected locations.

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